



Chemical vapor deposition of ordered TiO_x nanostructures on Au(111)



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ABSTRACT

The deposition of TiO_x ($x \leq 2$) structures on Au(111) by chemical vapor deposition (CVD) in ultrahigh vacuum (UHV) has been investigated with high-resolution core level photoelectron spectroscopy (PES), low-energy electron diffraction (LEED) and scanning tunneling microscopy (STM). Using titanium tetra-isopropoxide as single source precursor it is possible to form different TiO_x phases on the surface after deposition: at low coverages, we observe large two-dimensional (2D) honeycomb-lattice Ti₂O₃ islands with a (2×2) registry with the substrate. Higher coverages are dominated by the formation of three-dimensional (3D) TiO₂ structures. The TiO₂ structures are atomically well ordered provided that the deposition temperature is high enough (500 °C). The ordered structure exhibits a LEED pattern characteristic for a rectangular surface unit cell. By performing the deposition at different temperatures it is possible to tune the balance between the 2D and 3D phases: Growth at 500 °C significantly favors the formation of 3D TiO₂ islands as compared to growth at 200 °C and 300 °C.

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1. Introduction

Catalytic reactions promoted by Au nanoparticles deposited on the surface of a variety of different TiO₂ structures and surfaces have been explored extensively during the last decade [1–5]. The oxidation of CO on small, TiO₂ supported gold particles has been found to take place at remarkably low temperatures, down to 200 K [6]. Compelling evidence for a cooperative effect within the Au–TiO₂ system was put forward in a recent publication by the Yates group, in which they specifically point out Ti–Au dual sites at the particle perimeter as responsible for the catalytic activity [7]. The “inverse system”, TiO₂/Au(111), was also found to promote the water-gas shift reaction (WGS) ($\text{H}_2\text{O} + \text{CO} \rightarrow \text{H}_2 + \text{CO}_2$) [8]. Neither bulk gold nor titania is able to catalyze the WGS, while TiO₂ particles covering 20–30% of the Au surface showed an activity comparable to the one of Cu(110), a reference WGS catalyst.

The important properties of the TiO₂–Au boundary region have triggered several fundamental studies, aimed at controlling the synthesis and growth of titania particles on gold. In the majority of these, physical vapor deposition (PVD) of Ti metal and oxidation in O₂ atmosphere was used to produce titania structures on Au(111) [9–11]. Titania islands with hexagonal, triangular or needle-like shape were observed. Deposition and oxidation of defined-size Ti clusters were also employed [12],

producing clusters with hexagonal facets after annealing. Recently, Wu et al. conducted a thorough study of the development of ordered TiO_x structures on Au(111). The titania films were grown by post-oxidation of Ti at 600 °C [9]. For increasing Ti doses, they could obtain a wetting film with honeycomb (HC) structure, a pinwheel-like phase and eventually triangular islands. The oxidation of a Ti–Au alloy allowed for the production of rather well-defined TiO₂ crystallites exhibiting a line structure on the surface [13]. In an alternative approach denoted reactive layer deposition (RLAD), Ti was deposited on a layer of H₂O or N₂O and subsequent heating generated TiO_x structures [14,15]. Several coexisting structures were observed on the surface: hexagonal rutile-TiO₂ islands, octagonal lepidocrocite crystallites, ridge-like formations and a porous structure. The porous structure produced by RLAD bears a remarkable resemblance with the HC phase reported by Wu et al., although that paper claims that the pores had random diameters [11].

The previous studies thus reveal a complex behavior of the TiO_x/Au(111) system: two or more different structures often coexist on the surface and the preparation procedure influences significantly the structure and morphology of the TiO_x film [9–16]. A common trait among most of these works, however, is the finding of hexagonal titania islands. The latter were suggested to have the rutile structure, since the topmost layer exhibited a periodicity and step height compatible with rutile-TiO₂(100) [11,12].

A method that has not been used so far to grow TiO_x on Au(111) is chemical vapor deposition (CVD). In CVD a gaseous precursor reacts on a substrate, depositing a solid material. The deposition reaction is usually

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thermally activated, although other means to induce the precursor reaction exist. This technique offers the potential of coating finely structured and porous substrates by virtue of the effective penetration of the precursor molecules [17,18]. With respect to the TiO_x/Au system a particularly intriguing prospect is to use CVD to coat nanoporous gold, a nanostructured form of gold that exhibits considerable catalytic activity [19–22].

In the current work, we present results on the growth of titania nanostructures on Au(111) by decomposition of titanium tetraisopropoxide (TTIP), $\text{Ti}(\text{OC}_3\text{H}_7)_4$, a commonly used metal-organic precursor for CVD of TiO_2 . Two atomically ordered phases are found and characterized by high-resolution core level photoelectron spectroscopy (PES), low-energy electron diffraction (LEED) and scanning tunneling microscopy (STM). This is followed by an extensive growth study exploiting PES and LEED fingerprints of the phases. The growth series reveal that the balance between the phases changes with the deposition temperature. The study thus gives the first insight into the structural and morphological control attainable when using CVD for growth of ultrathin TiO_x films on Au(111).

2. Materials and methods

The experiments were conducted in ultra-high vacuum (UHV). The base pressure was always in the low 10^{-10} mbar range. The UHV chambers were equipped with LEED, ion gun and offered the possibility of heating the sample. PES measurements were carried out using synchrotron radiation at beamline I311 at the MAXII ring of the MAX IV Laboratory, Sweden [23]. The PES data presented in this paper were acquired in normal emission. Ti 2p spectra were measured using a photon energy of 590 eV, O 1 s spectra at a photon energy of 650 eV and Au 4f spectra at 220 eV. The kinetic energies of the photoelectrons were thus comparable, ranging from about 120 eV for O 1 s photoelectrons to about 135 eV for Au 4f photoelectrons. That is, their inelastic mean free paths (IMFPs) are also similar when travelling through the same material. PES was also used to check possible contamination originating from the decomposition of the precursor. No carbon impurities were observed upon growth at 300 °C and 500 °C, in accordance with previous growth experiments using TTIP [24], while they were noted upon growth at 200 °C. The binding energy (BE) scale of each spectrum was measured with respect to the Fermi level.

STM experiments were conducted at room temperature in the home laboratories at Uppsala University and at the Norwegian University of Science and Technology (NTNU) in Trondheim. In both cases an Omicron Variable-Temperature STM system and tungsten tips were used. A Au(111) crystal (Surface Preparation Laboratory) was used as a substrate. The clean Au(111) surface was prepared by means of sputtering and annealing (sputtering with Ar^+ ions at 1 keV for 20 min; annealing at 530 °C for 20 min; lowering the temperature from 530 °C to 430 °C in 5 min; annealing at 430 °C for 10 min), modifying slightly the procedure described by Biener et al. [16]. Sputtering and annealing cycles were repeated until only Au was detected by PES and the LEED showed a well-defined pattern of the herringbone (HB) reconstruction, which is characteristic of clean Au(111). The observation of large terraces presenting the HB reconstruction was also used to confirm that the surface was clean when STM was available. TTIP (Sigma-Aldrich, purity 99.999%) was stored in a glass tube connected to the vacuum chamber through a leak-valve. TTIP was dosed onto the sample in UHV using a stainless-steel tube positioned a few centimeters from the sample. The TTIP purification was carried out by freeze-pump-thaw cycles and the gas line was baked in order to remove water. For this purpose a sorption pump was also used. The TTIP pressures applied during deposition were between $1 \cdot 10^{-9}$ mbar and $5 \cdot 10^{-8}$ mbar.

3. Results and discussion

The influence of the substrate temperature and of the TTIP dose on the titania film structure grown by CVD was investigated by dosing increasing amounts of TTIP on the substrate at different temperatures. Two ordered titania structures could be found on the sample after deposition, depending on the deposition conditions. The titania films can be modified by post-deposition treatment and more structures can be produced. The latter will be described in a different paper, while the current work is focused on the as-deposited phases. We start with a presentation of the geometric structures of these phases on the basis of LEED and STM data in sec. 3.1. In the subsequent sections, PES results are used to characterize the chemical state of the two phases (sec. 3.2) and to analyze the morphological evolution of the film when performing CVD at different temperatures (sec. 3.3).

Growth series were conducted at three different substrate temperatures: the lowest temperature (200 °C) is close to the minimum temperature at which the TTIP precursor decomposes. At the next temperature (300 °C) decomposition is more facile but the growth is still expected to be reaction-limited [25]. At the highest temperature chosen (500 °C), the decomposition reaction is very fast making the growth flux-limited [25]. The formation of ordered structures during the growth was monitored with LEED. The focus is put on sub-monolayer coverages and ultrathin films (typically between 2 Å and 20 Å) partly covering the Au(111) surface; that is, situations where the synergy effects of the catalyst system are likely to be of importance.

3.1. Geometric structure of the ordered TiO_x phases

The first ordered structure obtained by CVD is the HC Ti_2O_3 phase. It is observed at low coverages at all three deposition temperatures. This structure has recently been observed upon Ti deposition at submonolayer coverage followed by post-oxidation at 600 °C [9]. According to the suggested model, Ti atoms sit directly on the gold surface, occupying alternatively a hexagonal close packed (HCP) or cubic close packed site (CCP) and the second nearest CCP or HCP sites, as depicted in Fig. 1A. This arrangement results in a layer of Ti atoms that form a structure of interconnected hexagons resembling an HC. The sides of the hexagons are aligned along the Au(111) $\langle 112 \rangle$ directions and measure 3.34 Å. Oxygen atoms are located in the middle of each side of the hexagons, presumably slightly above the Ti atoms. The unit cell of the HC structure has a (2×2) relationship with the one of the Au(111) surface.

STM images of the HC phase produced by CVD are shown in Fig. 2. At positive bias empty states are imaged. Since these are localized mostly on the Ti atoms (of formal charge $3+$) the bright features observable in Fig. 2B give the location of the Ti atoms. This imaging contrast is analogous to what has been reported for the rutile- $\text{TiO}_2(110)$ surface [26]. Images of larger sample areas (Fig. 2A) show that the HC phase forms large islands on the sample, reaching sizes of the order of 50 nm. The Au(111) HB reconstruction changes its orientation next to the HC islands, so that the soliton walls follow the perimeter of the latter. The apparent height of the HC islands was observed to change depending on the imaging conditions, consistent with the description provided by Wu et al. [9]. Simultaneous observation of a (2×2) LEED pattern (Fig. 1B) gives solid support for the proposed atomic structure model. The (2×2) superstructure spots were usually very sharp, confirming that the HC phase forms large ordered islands.

The second ordered titania structure is referred to as the Star phase, based on the LEED pattern shown in Fig. 3A. The pattern is comprised of three equivalent patterns rotated by 120°. The rectangular unit cell generating this pattern measures $23.8 \pm 2.3 \text{ \AA} \times 5.0 \pm 0.2 \text{ \AA}$.

Fig. 3B shows the LEED pattern generated by a phase with the lattice constants obtained as the average of these and of the one obtained by STM (see later in the text), showing that there is a very good agreement with the experimental LEED pattern.

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